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The ground state of the Fe_2 molecule

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The Fe_2 molecule is a typical transition metal dimer which has a rather large dissociation energy and a small bond distance compared with the inter-nuclear distance in the crystalline metal. We have investigated the Fe_2 molecule with multireference self-consistent-field (MCSCF) and multireference configuration interaction (CI) calculations. The dissociation energy (D_e), the equilibrium nuclear distance (R_e), and the zero-point frequency (ω_e) were calculated (with observed in parentheses) as 1.57 (1.30±0.22) eV, 2.06 (1.87 to 2.02) Å, and 260.9 (299.6) cm^{-1}, respectively. Thus the agreement between experiment and calculation is very satisfactory, and is a marked improvement on previous theoretical studies. The contribution of the *d* electrons to the bonding is important and a proper description of correlation effects among the *d* electrons is indispensable.

I. INTRODUCTION

In general, the equilibrium nuclear distances of the transition metal dimers are much shorter than the bond distance of nearest neighbors in the corresponding metals. For Fe_2, which is studied in the present paper, the internuclear distance (R_e) in an EXAFS study is 1.87 Å[1] in an argon matrix and 2.02 Å[2] in a neon matrix. This contrasts with the internuclear distance in solid Fe of 2.48 Å, a difference of 25%. The resonance Raman spectrum shows a fundamental frequency for the ground state of 299.6 cm^{-1}.[3,4] The electronic ground state of Fe_2 has been studied by several spectroscopic methods as well as theoretical studies; it is appropriate to consider the main possibilities first. First principles and the theoretical calculations described below suggest that three configurations for the ground state of Fe_2 can be considered, these have $(4s\sigma_g)^2$ in all cases, together with (a) $3d^{14}$; $3ds$ are totally bonding, (b) $3d^{14}$; $3ds$ are totally nonbinding, and (c) $3d^{13}+(4s\sigma_u)^1$, respectively.

The earliest experiments used to address the electronic structure problem were the Mössbauer spectrum;[4–6] this shows an isomer shift consistent with a smaller 4*s* population ($\sim 1.5e$) which is very near to that of solid Fe. The smaller 4*s* population of Fe_2 was also found by Shim and Gingerich[7] in the first *ab initio* study, who also showed that 50 excited states lay in the energy range 0–0.1 eV above their $^7\Delta_u$ ground state. The molecule was thought to have a single bond utilizing the $4s\sigma_g$ MO [category (b)].

The two photoelectron spectral bands of Fe_2^- under electron detachment spectroscopic conditions,[8] show vibrational structure with a common frequency and envelope. The first band is assigned to a transition between the ground states of both Fe_2^- and Fe_2, while the second is assigned as a transition to an excited state of neutral Fe_2. The absence of more bands is significant, since the free Fe atom has a number of low-lying states. This suggests that the atomic character is absent, and that the *d* electrons strongly contribute to the bonding. The authors[8] suggested that the anion to Fe_2 ground state was represented by the process: $(4s\sigma_g)^2(4s\sigma_u)^1(3d)^{14} \rightarrow (4s\sigma_g)^2(4s\sigma_u)^0(3d)^{14}$. The vibrational frequencies of the anion (250 cm^{-1}) and the ground state (300 cm^{-1}) (from the hot bands) were indicative of strong bonding in both cases.

The visible absorption spectrum of Fe_2 shows three bands, the lowest two of which show long progressions (195 and 200 cm^{-1}), which indicate that both the upper states are harmonic[9] in common with other related dimers.

Density functional[10] and X_α (Refs. 11,12) calculations indicate that the first configuration (d^{14}; totally bonding) is a good representation of the ground state; this is in contrast to post-Hartree–Fock calculations[7,13,14] which suggest that all three candidates given above are significant contributors. However, the density functional and X_α calculations used a single configuration state function (CSF), whereas the post-Hartree–Fock (HF) calculations were full valence CI, full valence MCSCF, or multireference CI. Thus the most elaborate post-HF calculations[13] used multireference configuration interaction calculations with a large basis set. The ground state of Fe_2 was found to be dominated by the $3d^{14}$ (totally; bonding) CSF; the correct bond distance of 2.02 Å was obtained, and the $4s\sigma_g$ MO was found to be nonbonding, in contrast to the results of Shim and Gingerich. Further, the calculations gave a positive binding energy of 0.94 eV relative to the Fe atom $3d^74s^1$ state, but failed to give the positive binding energies relative to the $3d^64s^2$ atomic ground state. This unsatisfactory situation is the focus of the present work, where more extensive calculations of the Fe_2 ground state are performed.

II. BASIS SET AND ATOMIC ENERGIES

A. Basis set

The basis set for the atom is a new (10*s*,6*p*,4*d*) basis of Slater type functions (STFs) constructed for this investi-

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TABLE I. Basis set for Fe_2 10*s*6*p*4*d* Slater type functions for Fe $(3d)^6(4s)^2\,{}^5F$.

s type							
1*s*	33.264 951	1*s*	24.726 647	2*s*	16.077 289	3*s*	16.086 963
3*s*	11.221 863	3*s*	5.460 147 7	3*s*	3.665 994 4	3*s*	1.532 852 8
3*s*	0.992 796 96	3*s*	0.745 049 50				
p type							
2*p*	18.584 132	2*p*	11.502 048	2*p*	9.294 214 8	2*p*	5.178 003 7
2*p*	4.531 958 8	2*p*	2.625 1436				
d type							
3*d*	10.091 785	3*d*	5.225 054 1	3*d*	2.711 898 6	3*d*	1.376 667 0

Correlating functions

*p*1	2*p*	1.487	for 3*d* electrons
*p*2	2*p*	1.009	for 4*s* electrons
*p*3	2*p*	0.504	for 4*s* electrons
*d*1	3*d*	0.0706	for 3*d* electrons
*f*1	4*f*	3.785	for 3*d* electrons
*f*2	4*f*	1.284	for 3*d* electrons

Comparison of Hartree–Fock and present basis

Basis set	Total energy (a.u.)	ϵ_{3d}	ϵ_{4s}
10*s*6*p*4*d*	−1262.4424	−0.64750	−0.25878
10*s*(6*p*+3*p*)(4*d*+1*d*)[a]	−1262.4429	−0.64699	−0.25830
12*s*8*p*6*d*[b]	−1262.4436	−0.64689	−0.25818

Energy separation between Fe $(3d)^6(4s)^2\,{}^5D$ and $(3d)^7(4s)^1\,{}^5F$

10*s*(6*p*+3*p*)(4*d*+1*d*)[a]	1.80 eV
12*s*8*p*6*d*[b]	1.80

[a]Additional three 2*p* and one 3*d* are STF's for the correlating functions. In order to determine the 2*p* STF's for 4*s* correlations, we first calculate $\langle 4s|r|4s\rangle$ and exponent of a single 2*p* is determined by the following equation: $\langle 4s|r|4s\rangle=(2n+1)/2\zeta$, where $n=2$ and $\langle 4s|r|4s\rangle=3.504$. The ζ is found to be 0.7135. Dividing or multiplying ζ of 0.7135 with $\sqrt{2}$ we get 0.504 and 1.009 listed in the table. By the same way we get two *p*-type correlating orbitals for the 3*d* electrons whose exponents are 2.974 and 1.487 and larger one is disregarded since it is close one ($\zeta=2.6251$) of the 2*ps* which construct atomic SCF. Tabulated 4*f* and 3*d* correlating orbitals are those for 3*d* electrons where one of 3*d* is disregarded since the calculated exponent 1.413 is close to one of 3*d* ($\zeta=1.3767$) of atomic SCF.

[b]See Ref. 15.

gation. The total energy for the Fe$(3d)^6(4s)^2\,{}^5D$ atomic state is −1262.4424 a.u., which is 0.0012 a.u. higher than the HF limit[15] (Table I). In addition to these STFs we add three 2*p*, one 3*d*, and two 4*f* STFs, as shown in Table I (footnote), in order to further allow for correlation effects among the 4*s* and 3*d* electrons. The SCF calculations on the (10*s*,6*p*+3*p*,4*d*+1*d*) atom now gave a calculated total energy only 0.0007 a.u. above the true HF ground state. We have also calculated the ${}^5F(3d^74s^1)$ state with the latter basis set; the energy separation between ${}^5D$ and ${}^5F$ is the same as in HF calculations where the exponents were optimized for the respective states; this shows the present set is flexible (see Table I).

B. Atomic energies

In the present paper we study the ground state of Fe_2 in the symmetry subgroup $C_{\infty v}$, using the ALCHEMYII code,[16–18] where this symmetry is fully utilized. However, in practice, the orbitals can be readily mapped onto $D_{\infty h}$ symmetry, and since it is conceptually more simple to use these symbols, hereafter we will use the full representation to discuss the electronic structure of Fe_2. We note that the SCF energy in $C_{\infty v}$ is slightly lower than that of the full atomic symmetry. Also, under these circumstances, the Fe_2 molecule dissociates into two $C_{\infty v}$ atoms if full CI calculations are not performed. The results of atomic CI calculations in $C_{\infty v}$ are listed in Table II.

III. THE MCSCF RESULTS

Following our previous work,[13] we have performed multireference-configuration self-consistent-field (MCSCF) calculations where all the 3*d* and 4*s* valence electrons are active and the full valence configurational space is active in the CI. The states selected were ${}^7\Sigma_u^+$, ${}^7\Delta_u$, and ${}^7\Delta_g$, and the MCSCF wave functions are spanned with 344, 512, and 509 CSFs, respectively. The lowest two or three solutions were solved by using the state averaging procedure for each state. Results of the MCSCF calculations are shown in Table III and also in Fig. 1. We have obtained two groups of the solutions [(a) and (b)]. In group (a), we began the sequence of calculations at the large nuclear distance of 10 a.u. The lowest and second lowest states of the respective symmetries of ${}^7\Sigma_u^+$, ${}^7\Delta_u$, and ${}^7\Delta_g$ are correlated to $(4s)^2(3d)^6\,{}^5D$. They have the electronic configurations of $(3d)^{12}(4s\sigma_g)^2(4s\sigma_u)^2$ and they give repulsive potential curves. Although we do not show the coefficients of

TABLE II. Results of CI calculation on energy separation between $Fe(3d)^6(4s)^2\,^5D$ and $(3d)^7(4s)^1\,^5F$ in $C_{\infty v}$.[a]

Basis function	$10s9p5d2f$ Basis								
Method	σ	π	δ					Energy (a.u.)	^5F–^5D (eV)
SCF	26	13	7					−1262.445 4	1.85
SD-CI[b]	Internal			External			Dimension		
	σ	π	δ	σ	π	δ			
Full-extl.[c]	2	1	1	9	10	6	46 859	−1262.583 73	0.81
332(NO)[d]	2	1	1	3	3	2	2 392	−1262.554 09	1.03
332(ANO)[e]	2	1	1	3	3	2	2 392	−1262.491 37	0.80
Expt.									0.88[f]

[a]Assumed configurations for ^5D and ^5F are $\sigma^2\sigma\pi^2\delta^3$ and $\sigma\sigma\pi^3\delta^3$. Total energies of ^5F for SCF, full-external SD-CI, 332(NO) SD-CI, and 332(ANO) SD-CI are −1262.377 55, −1262.554 06, −1262.516 61, and −1262.461 84 a.u., respectively.
[b]The electrons in 1–5σ, 1π, and 2π orbitals are treated as frozen orbitals in all CI calculations.
[c]In this SD-CI all the virtual orbitals are treated as external orbitals where one and two electron excitations are permitted.
[d]Using three σ, three π, and three δ natural orbitals in external space obtained from the CI with full-extl. given in (c) and exciting one and two electrons from the reference configuration, we have performed CI calculations on the respective states.
[e]We first performed a CI calculation where two electron excitations are allowed for three σ, three π, and three δ external orbitals and one electron excitations are allowed for the remaining orbitals. Using three σ, three π, and three δ natural orbitals in external space, we performed SD-CI which is designated as 332 (ANO; approximate NO).
[f]See Ref. 19.

TABLE III. Potential curve calculated by MCSF.[a]

The states correlated to $(3d)^6(4s)^2\,^5D$					
R (a.u.)	1st–$^7\Sigma_u^+$	1st–$^7\Delta_u$	1st–$^7\Delta_g$	2nd–$^7\Sigma_u^+$	2nd–$^7\Delta_u$
3.5	−0.648 77	−0.651 99	−0.654 64	−0.643 65	−0.641 21
4.0	−0.777 03	−0.769 51	−0.766 49	−0.767 07	−0.761 43
4.5	−0.828 87	−0.826 88	−0.824 47	−0.825 23	−0.821 26
5.0	−0.855 45	−0.855 39	−0.854 01	−0.850 42	−0.851 39
10.0	−0.891 24	−0.886 87	−0.887 42	−0.885 94	−0.885 03
∞	−0.890 88	−0.890 88	−0.890 88	−0.890 88	−0.890 88
The states correlated to $(3d)^7(4s)^1\,^5F$					
R (a.u.)	1st–$^7\Sigma_u^+$	1st–$^7\Delta_u$	1st–$^7\Delta_g$	2nd–$^7\Sigma_u^+$	2nd–$^7\Delta_u$
3.5	−0.670 89	−0.705 27	−0.678 52	−0.642 28	−0.630 81
4.0	−0.729 20	−0.744 61	−0.734 06	−0.723 81	−0.718 85
4.5	−0.755 06	−0.758 67	−0.755 08	−0.751 88	−0.750 21
5.0	−0.763 47	−0.762 52	−0.761 12	−0.760 09	−0.759 65
5.5	−0.764 00	−0.761 42	−0.760 69	−0.760 43	−0.760 37
6.0	−0.761 32	−0.758 79	−0.758 24	−0.758 50	−0.758 23
∞	−0.755 09	−0.755 09	−0.755 09	−0.755 09	−0.755 09

Calculated spectroscopic constant for the states correlating to ^5D				D_e relative to
State	R_e(Å)	TE (a.u.)[b]	ω_e (cm^{-1})	^5F (eV)
1st–$^7\Sigma_u^+$	2.791	−2524.764 51	149.2	0.26
1st–$^7\Delta_u$	2.696	−2524.762 61	133.0	0.20
1st–$^7\Delta_g$	2.744	−2524.761 54	143.7	0.18
2nd–$^7\Sigma_u^+$	2.780	−2524.760 99	148.4	0.16
2nd–$^7\Delta_u$	2.794	−2524.760 86	153.6	0.16

[a]For the first and second parts of the table −2524.0 a.u. is subtracted from the total energy.
[b]Interpolated value.

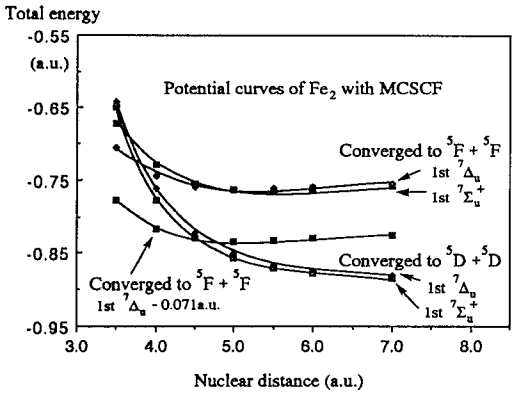

FIG. 1. The potential curves for Fe_2 calculated with MCSCF.

the important configurations, the atomic character holds for group (a) even at short bond distances, which makes the potential curves repulsive.

In group (b), we began the calculations at a bond distance of 5 a.u. and the solutions converged to the $(4s)^1(3d)^7\,{}^5F$ atomic states at infinite separation. The solutions found were completely different from those of group (a). They have a minimum around 2.7 Å, and the electronic configuration for these states is represented by $(3d)^{14}(4s\sigma_g)^2$. The lowest state is $^7\Sigma_u^+$ followed by a second $^7\Delta_u$ state. The results are the same as those of the full-valence like CI calculation of Tomonari and Tatewaki.[13] In Table IV, we select $^7\Delta_u$ and show the important configurations at 3.5(1.85), 5.0(2.65), and 10.0 a.u. (5.29 Å). The potential curve rises slowly at small internuclear distances (Fig. 1) where the correlation effects are expected to be important. Near the minimum the CSFs which describe the wave function at the separation limit, lose their importance, and others become dominant (Table IV). The $(4s\sigma_g)^2(3d\sigma_g)^2(3d\sigma_u)^1(d\pi_u)^4(d\pi_g)^2(d\delta_g)^3(d\delta_u)^2$ is the most important CSF at the shorter bond distances, where the number of the d electrons in the bonding orbitals is greater than that in the antibonding d orbitals. This is a contrast to the wave functions of group (a). Here, we add an important fact; before calculating the molecule with the $C_{\infty v}$ symmetry, we have performed full-valence CI calculations, using D_{2h} symmetry with a large GTF set. When we solved only the first solution we found that the most important electron configuration for the state was $(3d)^{13}(4s\sigma_g)^2(4s\sigma_u)^1$ which was parallel to that of Leopold and co-workers[14] and when we solved a couple of roots we found that these solutions had configurations near to $(3d)^{14}(4s\sigma_g)^2$; resulting eigenvalues were very close with each other. This suggests that when many states are energetically close, the iteration process of solving the Hamiltonian matrix, which requires several times larger trial vectors than those of the solutions, brings considerable remixings of the solutions. We feel that if such a small change (change in the number of solutions) affects the characteristics of the solutions, we need to take steps to make the contamination of the configurations as small as possible; we therefore use the $C_{\infty v}$ symmetry. Instead of converging to $(3d)^{12}(4s\sigma_g)^2(4s\sigma_u)^2$ or $(3d)^{13}(4s\sigma_g)^2(4s\sigma_u)^1$, which dissociates into $(3d)^6(4s)^2+(3d)^6(4s)^2$, or $(3d)^6(4s)^2+(3d)^7(4s)^1$ at the infinite nuclear separation, the first solution converged to $(3d)^{14}(4s\sigma_g)^2$. We feel that the solution with $(3d)^{14}(4s\sigma_g)^2$ is a strong extremum in the present full-valence configurational space; in order to obtain the group (a) of $(3d)^{12}(4s\sigma_g)^2(4s\sigma_u)^2$ we had to begin the calculation at a very large internuclear separation and had to use the initial guesses of the molecular orbitals strongly related to the atomic $(3d)^6(4s)^2\,{}^5D$ state. The configuration $(3d)^{14}(4s\sigma_g)^2$ at the shorter bond distances is reasonable since $3d$ electrons shield the nuclear repulsion more effectively than $4s$ electrons.

The two groups of the potential curves in Fig. 1 cross between 3.5 and 4 a.u. At infinite nuclear separation, the MCSCF approximation shows that the respective groups converge to two respective atomic Hartree–Fock states of ^5D and ^5F. Table II shows that the calculated separation of $(3d)^6(4s)^2\,{}^5D$ and $(3d)^7(4s)^1\,{}^5F$ by SCF is 1.85 eV while that from experiment is 0.88 eV,[19] a step which indicates that the orbital set and CI calculations which properly describe the separation of ^5D and ^5F are desirable.

TABLE IV. Important configurations for first $^7\Delta_u$ in MCSCF.

Configurations								Distances (a.u.)		
$s\sigma_g$	$d\sigma_g$	$s\sigma_u$	$d\sigma_u$	$d\pi_u$	$d\pi_g$	$d\delta_g$	$d\delta_u$	3.5	5.0	10.0
Important CSF's (coef. > 0.1)								coefficient > 0.1		
2	2	0	2	3	3	2	2	0.13	0.26	
2	2	0	1	4	2	3	2	−0.80	−0.51	
2	2	1	0	4	2	3	2	0.11		
2	2	0	1	3	3	2	3		−0.11	−0.13
2	2	0	1	3	3	2	3	−0.30	−0.32	
2	2	0	1	2	2	3	4		0.19	
2	1	0	2	4	2	2	3	−0.11		
2	1	0	2	3	3	3	2		−0.11	−0.13
2	1	0	2	3	3	3	2	0.25	0.29	
2	1	0	2	2	4	2	3	0.25	0.39	
2	1	0	2	2	2	4	3		−0.17	
2	1	0	1	3	3	3	3	−0.15	−0.33	0.15
2	1	0	1	3	3	3	3		−0.13	−0.16
2	1	0	1	3	3	3	3		−0.15	0.22
0	2	2	1	4	2	3	2		0.10	
1	2	1	0	3	3	3	3			−0.14
1	2	1	0	3	3	3	3			0.19
1	1	1	1	3	3	4	2			−0.27
1	1	1	1	3	3	2	4			0.27

Other 25 CSF's for 10.0 a.u. are not shown to save the space.

IV. LARGER-SCALE CI CALCULATIONS

First, we discuss the atomic states in the CI calculations where the molecule is dissociated. Since we will use σ, π, and δ orbitals in the molecular CI calculations, we calculate the atoms with these orbitals. The STF atomic basis was $10s9p5d2f$; the number of active atomic orbitals were 26, 13, and 7 for σ, π, and δ, respectively, and the 1–5σ $(1s,2s,3s,2p\sigma,3p\sigma)$, $1\pi(2p\pi)$, and $2\pi(3p\pi)$ were treated as a frozen core. The 6–$7\sigma(4s,3d\sigma)$, $3\pi(3d\pi)$, and $1\delta(3d\delta)$ were treated as internal occupied orbitals and the remain-

TABLE V. Electronic structure by larger CI for $^7\Delta_u$.

Reference configurations

Conf.	$s\sigma_g$	$d\sigma_g$	$s\sigma_u$	$d\sigma_u$	$d\pi_u$	$d\pi_g$	$d\delta_g$	$d\delta_u$	No. of CSF's
a	2	2	0	2	3	3	2	2	1
b	2	2	0	1	4	2	3	2	1
c	2	2	0	1	3	3	2	3	2
d	2	1	0	2	3	3	3	2	2
e	2	1	0	2	2	4	2	3	1
f	2	1	0	1	3	3	3	3	3

Information on the orbitals

Number of internal orbital

σ_g	σ_u	π_u	π_g	δ_g	δ_u
2	2	1	1	1	1

Number of external orbital

4	2	4	2	3	1

Total energies

R(a.u.)	CI(a.u.)	CI+Q[a](a.u.)	Weight of RCSF's (%)
3.5	−2524.980 72	−2525.033 98	83.74
4.0	−2524.995 54	−2525.039 92	84.73
4.5	−2524.994 54	−2525.030 40	86.46
5.0	−2524.985 61	−2525.016 88	87.40
∞	−2524.982 74	−2524.989 81	

Calculated spectroscopic constant for the states correlating to ^5D

	R_e (Å)	TE[a]	ω_e(cm^{-1})	D_e relative to ^5D (eV)
CI	2.220	−2524.996 60	219.5	0.38
CI+Q	2.058	−2525.040 34	260.9	1.57 (1.37)[b]
Expt.	2.02 or 1.87		299.6	1.30±0.20

[a]Interpolated value.

[b]1.57=TE(Fe_2,CI+Q)−2TE(Fe,CI);1.37=TE(Fe_2,CI+Q)−2TE(Fe,CI+Q).

ing orbitals (8–26σ, 4–13π, and 2–7δ) were treated as the external orbitals where one and two electron excitations were allowed. We call this full-external CI.

The reference was $(3d)^6(4s)^1$ and the dimension of CI was 46 859 for the ^5D atom and the total energy was −1262.5837 a.u. A similar calculation performed for the ^5F state gave an energy separation between ^5D and ^5F of 0.81 eV, which is very close to experiment (0.88 eV). Since the dimension of the Fe_2 molecular CI calculation was expected to be very large, some truncation of the size was sought, but one which did not lead to poor agreement with experiment. Using the resulting natural orbitals, we first truncated the external orbitals from (19σ, 10π, and 6δ) to (3σ, 3π, and 2δ) and performed a CI called 332(NO); the calculated $^5D/^5F$ energy separation remained satisfactory, with a value [Table II, 332(NO)] of 1.01 eV. This is to be expected, in view of the full-external CI and the use of the resulting natural orbitals. In the molecule, the above procedure is hardly performed since the dimension of CI becomes much larger because of larger number of the reference functions and available molecular orbitals. Next we performed a CI calculation which used three σ, three π, and two δ external orbitals and used the remaining orbitals (16σ, 7π, and 4δ) as higher orbitals where only one electron was able to be excited. Using the resulting three *s*, three *p*, and two *d* external natural orbitals, we performed CI calculations which are designated as 332(ANO) in Table II. The energy separation between ^5D and ^5F was 0.80 eV, again close to experiment and to the full external CI. This provided a good starting position for the molecular calculations.

An Fe_2 molecular calculation similar to the atomic 332(ANO) CI was sought, but it was also desirable to perform CI calculations which include the important configurations around the minimum, as well as the configurations responsible for describing the dissociation limits. However, this was expected to exceed our available computer facilities and a compromise had to be sought. The final selection was the six configurations (ten CSFs) given in Table V. The method of determining the correlating orbitals merits a brief discussion. In the first CI phase, the occupied orbitals mainly composed of 1*s*, 2*s*, 3*s*, 2*p*, and 3*p* were treated as a frozen core. The orbitals spanned mainly by 4*s* and 3*d* functions were internal orbitals; the four σ_g, two σ_u, four π_u, two π_g, three δ_g, and one δ_u (six σ, six π, and four δ in $C_{\infty v}$) were external orbitals; all other higher orbitals were included, but only single excitation was allowed. We first chose the $(s\sigma_g)^2(d\sigma_g)^2(d\sigma_u)^1(d\pi_u)^4(d\pi_g)^2(d\delta_g)^3(d\delta_u)^2$ configuration as a reference, which is the most important for $^7\Delta_u$ in the MCSCF calculation at short distances. The starting MOs are the MCSCF orbital of group (b) and the dimen-

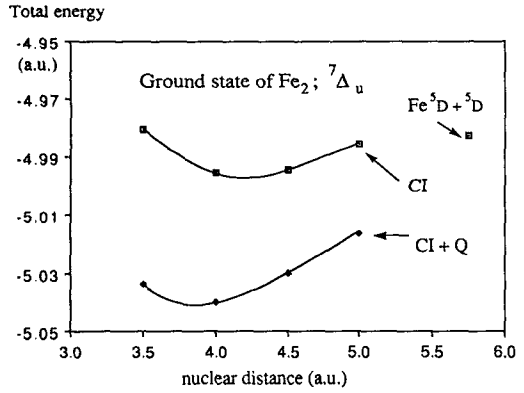

FIG. 2. The potential curve for the ground state of Fe_2 with large CI.

sion of this CI was 433 563. On the basis of the occupation numbers, we choose four σ_g, two σ_u, four π_u, two π_g, three δ_g, and one δ_u external natural orbitals, as the external orbitals for a larger CI. Finally, we performed CI with ten reference CSFs given in Table V. This CI has a dimension of 424 877, and is similar to the 332(ANO) CI for the Fe atom. The potential curves for the ground state with and without Langoff correction,[20] which are denoted as CI+Q and CI, are given in the same table and also in Fig. 2. The calculated dissociation energies relative to the ground state $(3d)^6(4s)^2\,{}^5D$ atoms by CI and CI+Q are 0.38 and 1.57 eV, respectively. The latter is close to the experimental value of 1.30 ± 0.20 eV.[21] One may wonder the larger effect of the quadruple excitations (Q). As shown in the table, the weight of RCSFs is small especially for the shorter bond distances, a step which suggests that the RCSFs are insufficient especially for the shorter bond distances and that the increase of the RCSFs would reduce the effect of Q; for example, the inclusion of $(3d)^{13}(4s\sigma_g)^2(4s\sigma_u)^1[(s\sigma_g)^2(s\sigma_u)^1(d\sigma_g)^2(d\sigma_u)^0(d\pi_u)^4(d\pi_g)^2(d\delta_g)^3(d\delta_u)^2$ given in Table III] may decrease the effects of Q. The equilibrium nuclear distance and ω_e are 2.06 Å and 260.9 cm^{-1}, respectively, to be compared with the observed values of 1.87[1]–2.02 Å[2] and 299.6 cm^{-1},[3] respectively. The theoretical calculation of R_e lies closer to that in the Ne[2] than the Ar matrix.

All these calculated results are in good agreement with experiment, and we feel that the present calculations give satisfactory theoretical explanations of the binding of Fe_2; the binding mainly arises from the correlation effects among the $3d$ electrons, confirming the conclusions given by Leopold and Lineberger[8] and Tomonari and Tatewaki.[13] The occupation numbers of the natural orbitals give the following electronic configuration for the ground state

$$(s\sigma_g)^{1.94}(d\sigma_g)^{1.77}(s\sigma_u)^{0.03}(d\sigma_u)^{1.18}(d\pi_u)^{3.52}(d\pi_g)^{2.39}$$
$$(d\delta_g)^{2.75}(d\delta_u)^{2.23}.$$

The sum of the occupation numbers for the d bonding orbitals (8.04e) exceeds that for the d antibonding orbitals (5.80e). In the external correlating orbitals $10\sigma_g$, 6, $7\pi_u$, and 3, $4\pi_g$, we found that the contribution of the f-STFs was rather large.

Finally we compare the present results with those of Tomonari and Tatewaki. The previous *ab initio* multireference CI calculation predicted that $D_e=-1.29$ eV relative to ${}^5D$, $R_e=2.02$ Å, and $\omega_e=448.5$ cm^{-1}. The difference in the spectroscopic constants comes from (1) a difference in the reference configurations—important configurations a and f in Table V were not included in the previous calculations and (2) a difference in the orbitals—no f-STFs in the previous calculations.

We have concentrated on the ground state properties around the minimum. As is apparent from Fig. 1,the ground state should be correlated with Fe $(3d)^6(4s)^2\,{}^5D$, and we disregarded configurations which lead ${}^5D$. We recall that in the MCSCF approximation the ground state smoothly dissociates to Fe $(3d)^7(4s)^1\,{}^5F$. The reference functions which are required to describe ${}^5F$ at infinite separation and some important configurations at the shorter bond distances such as $(s\sigma_g)^2(s\sigma_u)^1(d\sigma_g)^2(d\sigma_u)^0(d\pi_u)^4(d\pi_g)^2(d\delta_g)^3(d\delta_u)^2$ and $(s\sigma_g)^2(s\sigma_u)^0(d\sigma_g)^1(d\sigma_u)^1(d\pi_u)^3(d\pi_g)^3(d\delta_g)^3(d\delta_u)^3$ are also disregarded. Further investigations are necessary to describe adequately the whole of the Fe_2 potential curves.

V. CONCLUDING REMARKS

We have investigated the ground state of Fe_2 with MCSCF and multireference CI calculations. The calculated dissociation energy (D_e), the equilibrium nuclear distance (R_e), and the zero-point frequency (ω_e) are 1.57 eV, 2.06 Å, and 260.9 cm^{-1}, respectively, while the observed D_e, R_e, and ω_e are 1.30 ± 0.20 eV,[21] 1.87,[1] 2.02 Å,[2] and 299.6 cm^{-1},[3] respectively. The agreement is very satisfactory. It is important to describe the correlation effects among the d electrons effectively; the reference functions as well as the correlating orbitals need to be selected with care. We performed MCSCF calculations to obtain these reference functions and performed a fairly large CI calculation with a single reference function to define the necessary correlating orbitals. It was also found that the inclusion of f functions in all σ, π, and δ correlating orbitals is indispensable.

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